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PROJECT SQUID

SEMI-ANNUAL PROGRESS REPORT

APRIL 1, 1963

AERONAUTICAL RESEARCH ASSOCIATES OF PRINCETON, INC.
ATLANTIC RESEARCH CORPORATION
BROWN UNIVERSITY
UNIVERSITY OF CALIFORNIA (BERKELEY)
THE CATHOLIC UNIVERSITY OF AMERICA
CORNELL AERONAUTICAL LABORATORY, INC.
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THE PENNSYLVANIA STATE UNIVERSITY
PRINCETON UNIVERSITY
STANFORD RESEARCH INSTITUTE
UNIVERSITY OF VIRGINIA

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SEMI-ANNUAL PROGRESS REPORT

PROJECT SQUID

**A COOPERATIVE PROGRAM OF FUNDAMENTAL RESEARCH
AS RELATED TO JET PROPULSION
OFFICE OF NAVAL RESEARCH, DEPARTMENT OF THE NAVY**

This report covers the work accomplished
during the period 1 October 1962 to 31 March 1963
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April 1, 1963

**PROJECT SQUID HEADQUARTERS
DEPARTMENT OF AEROSPACE ENGINEERING
SCHOOL OF ENGINEERING AND APPLIED SCIENCE
UNIVERSITY OF VIRGINIA
CHARLOTTESVILLE, VIRGINIA**

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**FUNDAMENTAL INVESTIGATION OF NONSTEADY
AND NONEQUILIBRIUM FLOW****Cornell Aeronautical Laboratory, Inc. - Phase I****G. Rudinger, Phase Leader****Introduction**

This study deals with the extension of theoretical and experimental methods for the analysis of problems involving nonsteady and/or non-equilibrium flows. At present, two-phase flows are being investigated in which a gas carries along a large number of small particles that are evenly distributed over the cross section of a duct. The temperature and velocity of the particles cannot follow rapid changes of the conditions in the gas, and if the particles represent an appreciable mass fraction of the mixture, their response to the flow changes, in turn, affects the carrier gas. Considerable deviation from equilibrium may occur, and there exists a need to investigate such systems both theoretically and experimentally.

Discussion

As pointed out in previous progress reports, the passage of a shock wave through a suspension of small particles in a gas represents a flow

that lends itself particularly well to fundamental investigations. A study of the relaxation zone behind the shock wave revealed some interesting and unexpected features. For instance, the gas temperature immediately behind the shock wave may be higher or lower than the equilibrium temperature, and the transition may be monotonic or it may pass through a maximum or minimum value. In contrast, the final gas velocity, in shock-fixed coordinates, is always lower than the velocity immediately behind the shock, and the transition is generally monotonic. Although the particle velocity immediately behind the shock is considerably higher than the gas velocity, it could be shown that the particle drag cannot accelerate the gas even temporarily, except under extreme conditions that seem to be of little practical interest. The maximum particle drag appears where the difference between gas and particle velocity is greatest. Ordinarily, this condition occurs immediately behind the shock wave, but it was noted that, under certain conditions, the maximum drag may appear at some distance behind the shock.

As indicated in Ref. (1), a discontinuous shock front cannot be maintained if the shock velocity lies in the range between the frozen sound speed, that is the speed of sound in the gas phase alone, and the equilibrium sound speed which is always lower. In this case, there is no shock front at which initial temperature and velocity differences are established. Consequently, the original program for the computing machine, which evaluates the subsequent equilibration process, cannot be applied directly to dispersed shock waves. A linearization procedure was used to determine the early formation of the nonequilibrium zone and thus to find

starting values that may serve as boundary conditions for the subsequent evaluation of the entire relaxation zone. A machine program for these calculations has been completed and applied to a number of examples.

A paper on some of the material discussed in the foregoing was presented (2), and a complete manuscript is being prepared for publication.

General problems of nonsteady, two-phase flow require that six coupled, nonlinear, partial differential equations be solved. A wave-diagram procedure, based on the method of characteristics, was derived previously (3), and to illustrate the procedure, two examples have been worked out. The first example, discharge of a compressed suspension from a suddenly opened pipe, was completed during the preceding reporting period (3). The second example deals with the flow produced if a piston adjacent to a gas-particle mixture is impulsively accelerated to some velocity. A shock wave is immediately formed in the gas, while the particles, at first, remain at rest. As the relaxation processes become effective, the particles gradually accelerate, and the shock strength is modified. A machine program for this problem has been prepared and applied to a few cases. The most interesting result seems to be that the distance which the shock wave must travel to reach its final strength is much larger than the thickness of the relaxation zone behind a shock of constant strength. A paper on this work is also being prepared (4).

As noted previously (1), observations of the relaxation effects associated with shock waves passing through a suspension of solid particles in a gas hold the promise of yielding improved drag and heat-transfer correlations for the interaction between the gas and the particles. The

experimental work, started during the preceding reporting period, has been continued. A satisfactory method of feeding a known mixture of gas and particles through the driven section of a shock tube was developed, based essentially on the scheme reported previously (3). Attempts to determine instantaneous particle concentrations by means of light scattering or absorption were unsuccessful because particles settling on the windows produced erratic signals. It was then decided to try to record particle velocities by means of streak photography. A shock tube of square cross section (3 in. x 3 in.), having a test section with glass windows, was adapted for these experiments. One window was covered except for a narrow longitudinal slit illuminated by a parallel light beam. The slit was focused on the film in a rotating-drum camera. Movements of the particles, or rather of slight irregularities in the particle distribution, then appear as slanting lines on the film. At each end of the test section, a pressure transducer was mounted to measure the shock velocity by means of a microsecond counter. At one of these locations, the pressure was also recorded by means of an oscilloscope. To obtain records of the desired part of the transient flow with sufficient time resolution, the timing of a series of events had to be carefully controlled. Several automatic switches and electronic delay units were combined to a satisfactory recording system. A few records have been obtained but not yet evaluated. The next step in this program will be to find the best method to extract the desired information from such records and to estimate the reliability of the results.

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2. G. Rudinger, Some Properties of Shock Relaxation in Gas Flows Carrying Small Particles. Paper presented at the New York City meeting of the American Physical Society, January 22-25, 1963. (To be published, and issued as Project SQUID Report CAL-87-P).
3. Project SQUID Semi-Annual Progress Report, 1 October 1962.
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INVESTIGATION OF TURBULENCE

The Johns Hopkins University - Phase I

Leslie S. G. Kovasznay

Introduction

The research reported here is part of a long range program pursued under Project SQUID sponsorship for more than ten years currently under Contract Nonr 3623 (S-9).

The problems were actually investigated during the last few years and much of the earlier reported progress will not be repeated here.

Discussion

(A) Boundary Layer Transition. The transition experiment reported in Ref. 1 has revealed details of both the initial growth and the ultimate breakdown of periodic disturbances whose presence is predictable from

linearized theories. Since the later development of these disturbances was strikingly localized (high concentration of vorticity) it appeared logical to ask whether or not the same phenomenon would occur if the original disturbance would be also a spatially localized one.

During the present reporting period experiments were carried out with localized "puffs" produced in the laminar boundary layer. A spark was fired in a small chamber and through a small orifice the air was ejected through a hole in the wall. Detailed measurements with an array of hot-wires revealed that the actual flow configuration became more complicated than suspected. The small slug of air ejected forms a short duration high speed jet during its passage through the boundary layer but causes very little lasting disturbance there. A vortex ring forms outside the boundary layer that causes (though an image effect) a pressure pattern to develop over the plate. This pressure disturbance in turn excites boundary layer disturbances that cause the strongest velocity disturbances to occur in the inner portion of the boundary layer.

We have calculated the flow pattern of a vortex ring and the hot-wire traces are consistent with the theoretically predicted picture.

Presently a new method of injecting localized disturbances is under investigation. This new configuration will employ a short duration pulsed jet produced in the free stream and would cause the pressure disturbance

imposed from outside the boundary layer with the hoped for advantage that no parasitic flow disturbance would occur inside the boundary layer proper.

(B) Plasma Turbulence. Our long range objective is to produce and reliably measure turbulent fluctuations in an electrically conductive medium. The configuration considered is a shock tube with a square mesh grid as turbulence producing obstacle. Turbulence produced this way has been investigated in the non-conductive case. (Ref. 2)

The central difficulty with all plasma experiments is to produce a flow with a high enough magnetic Reynolds number (essentially the product of electric conductivity and of the linear dimension) is difficult.

After some experimentation with a "T-tube" (merely to learn techniques) a conical shock tube was chosen. Historically the conical shock tube was considered the most suitable plasma generator (1958-60) but as diagnostic techniques improved more and more undesirable characteristics were found. The most disappointing from our point of view is the rapid decay of the flow with distance from the conical section and this makes the production of homogeneous well-defined plasma "slug" almost impossible. The time spent with the conical shock-tube was not wasted however. We have acquired the ability to use streak camera, Kerr cell shutter and have even a moderate experience with magnetic probes.

New shock configurations are being investigated now by other plasma research groups. Of these, one financially feasible solution is offered by "Fowler's shock tube" (Ref. 3). The discharge occurs between ring electrodes separated by insulating sections. The electrodes are positive and negative in alternating order. All condensers are discharged simultaneously thus producing a high temperature, high pressure gas volume similar to the conventional aerodynamic shock tube, and shock decay is expected to be much slower than with conical shock tubes.

Such a shock tube has been built with 8 sections ($7.5\mu\text{F}$) each and is under check-out. In the next few months attempts will be made to produce a turbulent flow in this shock tube. The conical shock tube still may be used as a secondary source of plasma.

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FUNDAMENTAL STUDY OF DYNAMICS OF GASES AND PLASMAS

Aeronautical Research Associates of Princeton, Inc. - Phase 1

Dr. Guido Sandri, Phase Leader
Mr. Roger D. Sullivan, Associate Consultant
Dr. Theodore F. Morse, Senior Research Engineer
Prof. Edward A. Frieman, Consultant

Introduction

The aim of our program is a complete dynamical theory of gases (including plasmas) which starts from the fundamental Liouville equation of classical mechanics (1). Our results to date are largely concerned with the theory of a single component gas both with regard to the kinetic (2,3,4,5) and its hydrodynamic behavior (6). The study of gaseous mixtures is now in active progress (7,8).

Discussion

1. Higher order kinetic equations. The mathematical apparatus of our new method (method of extension) has been improved and deepened so as to allow for a detailed investigation of the higher order kinetic equations. The problem was first investigated

in reference (1) and the results have been considerably extended by means of a graphical technique (9) and an integral method for summing to all orders particularly important classes of graphs (10).

The outstanding result of this investigation is that a purely kinetic description, that is one in which the single-particle distribution function F^1 is determined by its initial value only, of three-body phenomena is not possible. Thus for the study of reactions one must resort to a theory relying on more general principles than those allowed for by a purely kinetic description of gases. A number of results along these lines have already been obtained (11) and are being prepared for systematic presentation.

2. Equipartition equations for homogeneous mixtures. The extension of our theory for a single component gas to mixtures presents many important problems. Morse has investigated the equipartition times for energy and momentum under the assumption that the light components become maxwellian in their velocity distribution prior to equipartition (7). A derivation of equipartition equations with the method of extension has also been given (8). With this method it is possible to establish the limits of validity of the equipartition equations themselves.

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RESEARCH ON THERMODYNAMIC AND TRANSPORT
PROPERTIES OF GASES AT HIGH TEMPERATURES
AND PRESSURES

Brown University, Providence 12, R. I.: III

Prof. J. Kestin, Div. of Engineering
Prof. J. Ross, Dept. of Chemistry
Dr. J. H. Whitelaw
Mr. A. Nagashima
Mr. R. DiPippo
Mr. R. Wood
Mr. T. F. Zien
Dr. M. Afzal
Mr. C. Pyun
Dr. S. Kim

Introduction

The work on the measurement and calculation of transport properties continued under joint sponsorship of Project Squid and the National Science Foundation, the broad objective remaining unchanged.

Discussion

A. First torsional viscometer. Measurements on the viscosity of carbon dioxide in the critical region have been completed. Owing to the difficulties associated with maintaining a state close to the critical, it was

decided to perform the measurements twice independently. The two series so obtained show excellent agreement. Contrary to the work of A. Michels, A. Botzen and W. Schuurman, it is found that the viscosity of carbon dioxide does not increase by a factor of 2 near the critical point, there being an increase of about 10%. Corrections due to density stratification have been estimated, and it is shown that they are not very large and do not alter the general conclusions.

This work has been described in a Squid technical report "Viscosity of Carbon Dioxide in the Neighborhood of the Critical Point", by J. Kestin and J. H. Whitelaw.

Work has begun on the determination of the viscosity of air from room temperature to 300°C and over a range of pressures from 1 to 130 atm. Simultaneously, the effect of humidity up to saturation on the viscosity of air in that range is being investigated.

B. Second torsional viscometer. The very accurate measurements on the viscosity of inert gaseous mixtures have continued. The initial work has been described in two Squid technical reports, "The Viscosity of Argon-Helium Mixtures" by H. Iwasaki and J. Kestin, and "The Viscosity of Argon-Ammonia Mixtures" by H. Iwasaki, J. Kestin and A. Nagashima".

Measurements have been completed on the viscosity of argon-neon mixtures, and work is in hand on a precise determination of the relative viscosity of H_2 , D_2 and HD with a view to determining the differences in the intermolecular

force potentials of these three, simple molecules.

The results of these measurements are now being compared with calculations; the object of these is to test the semi-empirical mixing rules which play an important part in plasma calculations.

C. Third torsional viscometer. The manufacture of parts has been essentially completed, and the viscometer has been assembled in a preliminary way. The quartz strand has been calibrated for internal damping in a vacuum and tested up to 800°C . This preliminary work indicates that it ought to be possible to make preliminary measurements at least up to 800°C and possibly up to 1000°C during the next six months. The expected precision is still 0.1%.

D. Capillary flow viscometer. Final calculations and evaluation are being made on the viscosities of CH_4 , H_2 , D_2 , and CO obtained from measurements in the capillary flow viscometer at 7 temperatures in the range -50°C to 150°C and as a function of pressure at each temperature.

Plans are being made to extend the range of temperatures in the present viscometer to -150°C . This requires construction of a new low-temperature thermostat for the capillary cell. A simple design which makes use of a controlled spray of liquid nitrogen unto a separately controlled thermostat is thought to be sufficient. The extension of viscosity measurements as a function of density to lower temperatures is of importance. No such data now exist, but are sought to test further empirical correlations and future theories of transport.

E. Theory of viscosity of dense gases. The viscosity of a dense gas determined from experiments can be written as a sum of two functions, one dependent on temperature only, the other dependent on density only. This empirical correlation is not predicted by the Enskog theory, an extension of the dilute-gas transport theory to dense gases for the molecular model of hard spheres. We are investigating a theoretical justification of this relation by inquiring into the effect of attractive rather than repulsive forces on the first density correction to the viscosity. A model of molecular association proposed by Stogryn and Hirschfelder has been used to predict, so far in a very crude analysis, not only the density and temperature variation cited above, but also the variation of the viscosity with density as a function of potential energy parameters. Further work on this approach is warranted.

F. Theses. Mr. T. F. Zien is completing his Master's thesis entitled "The Viscosity of Carbon Dioxide in the Neighborhood of its Critical Point" and hopes to graduate in June 1963.

Mr. R. DiPippo is working on his Master's thesis entitled "Correlations of Viscosity of Gaseous Mixtures." and hopes to present it either in June or in September 1963.

G. Meetings. Prof. J. Kestin has been appointed to the Organizing Committee of the Sixth International Conference on Properties of Steam to be held in New York City at the United Engineering Center from October 7th through October 11th, 1963.

Prof. J. Kestin has been invited to deliver lectures at Purdue University and at the Hartford Center of Rensselaer Polytechnic Institute. He has also been invited to deliver a course of lectures to staff members and industrial representatives at the Norges Tekniske Høgskole in Trondheim, Norway during the month of August 1963.

Prof. J. Ross attended the XII, International Solvay Congress in Brussels, Belgium and presented a lecture on the study of chemical reactions in crossed molecular beams. Invited lectures were also given at the University of Chicago, University of Illinois, and Pennsylvania State University.

PROPERTIES OF TWO-PHASE FLOW - ELECTRIC PHENOMENA

University of Illinois - Phase 1

S. L. Soo
J. A. Hultberg
G. J. Trezek
R. C. Dimick

Introduction

Our studies on the electric charge phenomena in a gas-solid suspension concern two aspects: Electrification of solid particles due to surface interaction; and thermal electrification due to thermionic emission of solid particles at high temperatures as limited by space charges.

Our studies have shown that the concentration and mass flow distributions of solid particles in a duct is strongly affected by the charges carried by the solid particles due to impact with the wall; and such distributions, of course, affect friction and heat transfer from a wall to a gas-solid suspension. Thermal electrification further explains the large extent of electron concentration in a gas-solid suspension at moderately high (2000° to 3000° K) temperatures. The resultant electrical conductivity, of course, bears significance to the operation of an MHD accelerator with intentionally or unintentionally added solid particles.

Our study on the removal of electrons by charged solid particles points to the possibility of reducing the attenuation of radio waves by an ionized gas.

Discussion

In connection with the electrification by surface interaction, a study was made on the distributions of concentration, mass flow, and velocity of solid particles with a fiber-optic probe and an electrostatic ball probe. The fiber-optic probe measures concentration distribution of solid particles by light scattering in a gap between a miniature light source and a photocell. The measurement of mass flow of solid particles is made through the recognition of electrification of solid particles by impact with the wall of the duct, and this measurement is made possible by accurate measurement of current down to 10^{-13} ampere. The probe measurements were normalized from measured total flow rate and over-all average concentrations. Dividing local concentrations into mass flow gives the local particle phase velocity. Through these measurements, concepts concerning these distributions and electrostatic charges on solid particles were furthered and substantiated. Due to the induced electrostatic charge on solid particles, concentration distribution is higher toward the wall, even for particles below 50 microns in diameter. Results confirm the trend and improve the accuracy of earlier measurements by impact counter systems and evaluation by theoretical procedure (1, 2), and recent measurements by a capacitance probe by van Zoonen (3). The relation between electrostatic charge on solid particles and diffusivity of solid particles (4), and the difference between static loading and mass flow ratio of phases were pointed out and proven. The nature of the concentration, mass flow, and velocity distributions of solid particles is such that the concentration increases toward the wall of the pipe, mass flow decreases toward the

wall, and velocity is less or equal to that of the stream at the core, but is finite at nearly 20% core velocity at the wall in the range studied. The fluid follows nearly $1/7^{\text{th}}$ velocity law, but the particles follow nearly linear with distance from the wall to nearly $2/3$ power with slip at the wall. The trend of the concentration distribution is shown to be definitely due to electrostatic repulsion of the charged particle cloud and diffusivity from the wall due to concentration gradient established. Experiments were carried out with glass and magnesia particles in a brass pipe.

Solid particles become charged due to thermal electrification at temperatures of 1000° to 3000° K (5). This explains the high electron concentration in a rocket jet with metallized propellant and the higher than theoretically predicted conductivity in an MHD generator with combustion products. It was recognized that thermal electrification is not synonymous with ionization of solid particles (6). In a static system of a solid particle in a given volume of evacuated space, thermal electrification produces a system including a charged solid particle surrounded by an electron cloud, forming a neutral system. Ionization of this system can be produced by an electromagnetic field or scattering by an external electromagnetic field or scattering by gas molecules. Therefore, thermal electrification of a turbulent gas solid suspension gives rise to charged solid particles with a certain amount of free electrons due to scattering by the turbulent field. Significant electron concentration occurs in a gas-solid suspension at around 3000° K, even with helium as the suspending gas. Of course, the concentration of helium ions is negligibly low.

Preliminary experiments on thermal electrification use accurately metered amounts of solid particles such as iron heated by means of a propane flame. In this case the effect of combustion is unavoidable. Accurate measurement was made possible by a triode configuration, an extension of the principle of an ionization gauge. Here the grid shields the field due to the solid particles. With blowing down of this jet into a vacuum at 20 mm Hg of 1.3 g/min. of 50-micron iron particles heated to 1000°C , the electron concentration was measured to the $3 \times 10^9/\text{m}^3$. The iron concentration was $3 \times 10^{11}/\text{m}^3$ for $10^5/\text{m}^3$ of iron oxide particles. Therefore, in the absence of turbulence or other large external field, a large number of electrons move along the side of the charged solid particles, because here the turbulent field is absent. The solid particles were not deflected by the given electric field in the distance traveled, due to their inertia. To avoid the complications due to combustion, we are now experimenting with solid particles heated by an electric arc to 3000°K .

Removal of electrons from an ionized gas by using positively charged solid particles is shown to be capable of reducing the electron concentration in an ionized gas from $10^{17}/\text{m}^3$ to $10^{14}/\text{m}^3$ with $10^5/\text{m}^3$ of 1-micron zirconia particles charged to 0.5 coulomb/kg. In our experiments with injection of positively charged solid particles (200 mesh alumina) at 1.3 g/min. into a glow discharge at 8 mm Hg pressure, it was possible to reduce electron concentration considerably; the arc current was reduced from 30 ma to nearly zero. Experiments being planned include charging of solid particles by a corona charging system to a well-defined magnitude.

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THERMAL CONDUCTIVITY OF GASES AND LIQUIDS
OVER A RANGE OF TEMPERATURES AND PRESSURES

Massachusetts Institute of Technology - Phase 2

Frederick G. Keyes, Phase Leader

Introduction

The Progress Report of October 1, 1962 gave a description of the effort directed to correlation of the thermal conductivity data obtained for a number of substances listed under "Discussion". The correlation and tabulation is essential for convenience of use and, in course, the data of the literature is being evaluated and algebraic formulae devised by means of which extrapolation may be made into regions at present inaccessible to direct measurement. As already stated in the preceding report, viscosity data and heat capacity data have been culled from the literature which makes possible the calculation of Prandtl numbers useful for dealing with fluid flow problems.

Discussion

A paper on the results of the thermal conductivity of steam is nearly ready to send to the editor of the Journal of Heat Transfer. An important aspect of the conductivity is the effect of pressure and a quantitative understanding of the characteristics of the effect relative to density and temperature. Based on the Squid program measurements in the saturation region, a correlation equation for the pressure effect for steam has been formulated which reproduces recent Russian data to 500 C and to 500 atm.

Correlation has been completed to 1000 atm for carbon dioxide to 700 C. The data measurements were made at the French Laboratoire des Hautes Pressions at Bellevue. Similar formulations are in progress for all substances measured under the Squid program and taken from the scientific literature.

A STUDY OF FLUID FLOW WITH SUSPENDED PARTICLES

Princeton University - Phase 12

R. Eichhorn - Phase Leader

J. F. Muir

R. A. Shanny

Introduction

Three separate studies have been undertaken since the inception of this research. The first, lift forces on particles in a velocity gradient has been completed and a report will appear in the near future. The two remaining studies are uncompleted and are discussed below.

Discussion

Turbulent flow of a gas-solid suspension. As described in earlier progress reports, the primary effort has been directed toward developing instrumentation to determine the flow properties of the mixture. Of late, we have concentrated on a fiber optic probe employing two glass fibers. With this device, it is possible (in principle at least) to determine the complete longitudinal particle velocity distribution function. The early versions of this probe suffered either from severe erosion by the particles (200 micron glass beads) or an inability to maintain proper alignment of the fibers. Both of these features have been improved in the latest probe design, which provides as well for a relatively simple replacement of the fibers.

Compressible flow of a gas-liquid mixture. A report (1) on this study is being readied for distribution. Reported are the results of measurements of pressures and velocities for flow of a water-air mixture in a convergent-divergent nozzle. The nature of the results were summarized in the last progress report.

Current efforts are directed toward planning additional experiments, particularly with an eye to the effects of bubble size and liquid viscosity. Further efforts will also be expended toward understanding the fluid dynamic properties of supersonic gas-liquid flows.

The experimental results mentioned above have indicated that the ratio of the volume fraction to the volume flow fraction may be treated as a constant, and further that this constant is the same as has been reported for widely different flow geometries (2). This fact permits an analysis of compressible flow in varying area channels. Such an analysis is presently underway.

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THEORY OF FAST REACTIONS

University of California (Berkeley) - Task Order 1

Michel Boudart, Chief Investigator

Introduction

This program comprises a theoretical and experimental study of the decomposition of ozone in shock and detonation waves. Special emphasis is to be placed on the possible production and relaxation of vibrationally excited oxygen molecules and on the nonclassical kinetic reactions involved.

Discussion

When the activation energy E of chemical reactions becomes small as compared to RT , the conventional theory of reaction rates may fail, firstly, because the reactants may not exhibit a Maxwell-Boltzmann distribution of energy, and secondly, because the transmission coefficient, i. e. the probability of reaction for a system that has reached the transition state, may well

fall below unity. This latter question is being attacked theoretically by methods outlined by M. Boudart and R. De Vogelaere (1), following a suggestion of E. P. Wigner who pointed out the similarity of this problem to that of the behavior of ionized particles in the magnetic field of the earth.

It appears that ozone is a system in which anomalies due to non-equilibrium distribution of energy among the reacting components might well be observable (2). Consequently, experimental investigation of detonation waves in ozone is suggested. Since one of the reactions involved in the ozone decomposition has a low activation energy, at detonation temperatures, E/RT is small enough that the considerations of Boudart and De Vogelaere (1) may well apply with a resulting low transmission coefficient. Furthermore, if vibrationally excited oxygen molecules are produced, one wonders whether oxygen has time to relax during the time of reaction in the wave. Although this may well be so in the presence of oxygen atoms, it is difficult to know for sure. Experimental study of mixtures of ozone with oxygen and inert gases will be undertaken in the detonation tube with the hope of finding out more about the energy transfer processes of the system if they are important. If they are not important, this negative result will be significant in itself. Indeed, if ozone does not exhibit such anomalies, it may well be inferred, with due caution, that no other system will.

Since this research program was initiated on 1 October 1962, no reportable results are as yet available. The theoretical calculations are

currently underway, and results should be available for reporting in the next Project SQUID Semi-Annual Progress Report.

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KINETICS OF ELEMENTARY REACTIONS

The Catholic University of America - Phase No. 1

B. deB. Darwent - Principal Investigator

A. L. Flores - Investigator

Introduction

Although there is some information on the rate constants and activation energies of reactions involving the less reactive halogens (Cl_2 , Br_2 , I_2) there is essentially no quantitative information concerning the reactions of the most reactive of the halogens (F_2).

From the practical point of view, there are many indications that the system $\text{F}_2 + \text{H}_2$, under optimum conditions, has a higher specific impulse than any other chemical system. Some knowledge of the kinetics of the reactions of F atoms with H_2 and of H atoms with F_2 will be of interest to all concerned with propellants.

The photolysis of NOF will be used as the source of F atoms, thus avoiding the occurrence of long chains which are present in the reactions of F_2 . The principal difficulty is the construction of an apparatus suitable for precise kinetic measurement of fluorine atom reactions. We propose to use teflon as the material for this apparatus and fluorite as the window material.

Discussion

There is very little real progress to report during the first year of this project. The following work has been carried out:

- (a) Development of a method for preparation of NOF - found to be unnecessary by the discovery of a commercial source of the gas.
- (b) The possibility of using pyrex as a material for the reaction system was investigated. The reaction of NOF with pyrex was found to be much too fast, even when every precaution was taken to dry the materials thoroughly.
- (c) A stirred reaction vessel, with a fluorite window, has been constructed from teflon and shown to be free of leaks.
- (d) Several samples of teflon tubing have been obtained and tested. All were found to be much too porous for use in the vacuum system. New samples stated specifically to be vacuum tight, have been obtained and found satisfactory.
- (e) A teflon pressure measuring device has been constructed from teflon tubing. It has a reasonable sensitivity of approximately 1 mm deflection per centimeter change in pressure. Improvement in the sensitivity is being attempted.
- (f) All-teflon valves have been designed, fabrication and tests are being held up pending the arrival of a sample of a commercially available valve.
- (g) The reaction of NOF with glass has been found to be very much faster than with H_2 or isobutane.

INVESTIGATION OF REACTION KINETICS
IN HIGH-TEMPERATURE GASES

Cornell Aeronautical Laboratory, Inc. - Phase 2

George H. Markstein, Phase Leader

Introduction

This study is concerned with kinetics and mechanisms of reactions in high-temperature gases. The specific system now under investigation is the reaction of magnesium vapor with oxygen. The methods employed in the work are suitable adaptations of the dilute-diffusion-flame techniques that have been successfully used for other reacting systems.

Discussion

During the present report period, a survey paper on metal combustion (1) was prepared and presented at the Annual Meeting of the American Rocket Society. From this review of the present state of the field it was concluded that, compared to the present knowledge of combustion of conventional fuels, the burning of metals is as yet poorly understood. The formation of condensed-phase products in metal flames was found to be primarily responsible for the current lack of understanding. One cause of

difficulties is the absence of reliable thermodynamic data, particularly on condensed-phase and vapor-phase oxide species.

The foremost uncertainties arise, however, because the presence of condensed phases implies the predominant participation of heterogeneous reactions in metal combustion. Ignition of metals is always regarded as a surface reaction. Difficulties in understanding the ignition process have been encountered especially with those metals that form a protective oxide layer.

After ignition, the burning process may either continue to take place on the surface of a usually molten oxide layer covering the metal, or the reaction may occur in the surrounding vapor phase. Even in the latter case, heterogeneous reactions on the surface of growing oxide-smoke particles may play a predominant role. Knowledge of reaction mechanisms and kinetics for either surface or vapor-phase burning is as yet almost nonexistent.

The work on the magnesium-oxygen dilute diffusion flame performed under this phase, described in preceding semi-annual reports and in a recent paper (2), constitutes a first attempt to determine the rate and mechanism of a metal-combustion reaction of interest in propulsion. The data thus far obtained by photographic photometry favored a unimolecular rate law. A unimolecular rate constant of $(2.5 \pm 1.2) \times 10^3 \text{ sec}^{-1}$ was determined for an estimated flame temperature of 1000°K. On the basis of the rate data, of spectroscopic evidence, and of thermodynamic arguments, it was concluded that at the low pressures and temperatures prevailing in these flames the oxidation took place predominantly as a

heterogeneous reaction on the surface of growing oxide particles. A tentative mechanism of this surface reaction has been proposed (1, 2).

One of the as yet unsolved problems in this work concerns the determination of the temperature of the flame gases. The estimated flame temperature seems too low for using the line-reversal technique or other optical methods. Fine-wire thermocouples have been used successfully for measuring the temperature of flame gases that contained reactive species, by rendering the wire surface noncatalytic (3,4). However, since thus far it has been found impossible to prevent the formation of magnesium-oxide deposits on any surface introduced into the flame zone, it seems at present impossible to produce a surface that would be non-catalytic for the Mg-O_2 reaction.

Thus, the use of thermocouples undoubtedly would not yield the true temperature of the flame gases. It seemed, nevertheless, of interest to use the thermocouple method, since it was felt that it would give at least an upper limit for the flame temperature, and moreover, it might enable measurement of local rates of the heterogeneous reaction on the wire surface. Preliminary runs, in which iron-constantan thermocouples, made by electrical butt-welding of No. 40 wires, were introduced into the flame, have given as yet somewhat erratic results. The thermocouple readings tended to drift upward as the deposit on the wires grew, although one would expect constant readings, since the heat input by surface reaction and the losses are both proportional to surface area. Readings in individual runs performed under apparently identical conditions differed appreciably, and were in some runs higher and in others lower than the vaporizer

temperature. The highest thermocouple reading so far obtained was 1083°K, so that the previous estimate of flame temperature does not seem too unreasonable. It was verified qualitatively that the thermocouple readings were related to the oxidation reaction, since they responded in the expected direction to changes of oxygen flow. The results so far obtained are insufficient for deciding whether useful quantitative information can be obtained by the thermocouple method.

Concurrently with the continuing experimental work, an analytical study of a model of the dilute diffusion flame supported by heterogeneous reaction has been initiated. The treatment carried out thus far is based on the assumption that nucleation of oxide particles occurs only in a narrow innermost region of the spherical flame. From this region outward, no new particles are formed, so that the particle-size distribution changes only owing to growth of the particles by surface reaction. Under this assumption, one obtains the greatly simplifying result that the distribution about the mean particle diameter remains constant. Correspondingly, the expressions for the total volume and the total surface area of the particles contained in unit gas volume are simplified appreciably. When these expressions were inserted into the equation of conservation of nozzle reactant, and into an equation relating rate of particle growth with rate of surface reaction, a system of two coupled nonlinear differential equations was obtained. For large radius, asymptotic solutions were obtained that were identical with the solution of the usual linear equation of the dilute diffusion flame (2). Numerical solutions of the nonlinear system were derived by integrating from large towards smaller values of the radius,

with the asymptotic solutions as starting values.

The results showed that deviations of the solutions from those of the linear equation are smallest when the particle nucleation occurs very close to the nozzle; the deviations increase as the region of nucleation moves outward. Nonlinearity effects are most noticeable for monodisperse particles and decrease with increasing width of particle-size distribution. Since the experimental results gave no indication of nonlinearity (2), the analysis seems to imply that nucleation occurred very close to the vaporizer orifice, and that the size distribution may have been broad. Since the assumption that nucleation is restricted to a narrow zone seems unrealistic, it is planned to continue the analysis under less restrictive assumptions.

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REACTIONS OF IONS AND ELECTRONICALLY EXCITED
SPECIES WITH ATOMS AND MOLECULES IN THE GAS PHASE

Humble Oil and Refining Company Nonr-3623(S-18)

J. L. Franklin, F. H. Field, and M. S. B. Munson

Introduction

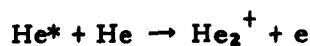
The program has for its principle purpose the study of ion-molecule reactions and chemi-ionization reactions in gases. The instrument employed is a mass spectrometer capable of operating at pressures up to about $1/2$ mm of Hg. in the ionization chamber. During the period just completed two specific studies have been in progress. One of these has been a detailed investigation of the reactions leading to the formation of rare gas diatomic ions. The homonuclear diatomic ions in the rare gases have been known for a number of years and it has been established that they are formed by chemi-ionization reactions. A few heteronuclear rare gas diatomic ions have also been reported in the last few years. We have established that diatomic ions are formed from all combinations of helium, neon, argon, krypton, and xenon, and the present investigation has shown that all of these are formed by chemi-ionization processes.

A program has been initiated for the purpose of identifying the principle ion-molecule reactions occurring in the various light hydrocarbons at elevated pressure in the mass spectrometer. A rough preliminary study about a year ago indicated that very extensive reactions occurred at pressures in the order

of a few tenths mm with the light paraffins through butane and the light olefins through the butenes. The present study has as its purpose a more careful and detailed investigation in which we hope to identify and measure the rates of the various reactions involved. In the course of this we hope to measure the rates at which certain metastable ions are formed by decomposition of unstable complexes in the analyzer tube.

Discussion

Rare Gas Diatomic Ions. The appearance potentials of the various rare gas diatomic ions have been measured and the results are given in Table I along with those of other investigators. Where comparison is possible, our results agree reasonably well with those of other workers. It will be noted that appearance potentials of HeXe^+ was not determined. This ion was observed but the intensity was too small to permit a satisfactory measurement of its appearance potential. Pressure studies were made with a few of the diatomic ions and in all cases showed that a bimolecular second-order rate process was involved. The intensities were not dependent upon repeller voltage and accordingly we concluded in all cases that the ions were formed by chemi-ionization typified by the following:



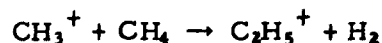
The data in Table I show a couple of rather surprising values. It is especially noteworthy that the appearance potential of HeAr^+ falls above the ionization potential of argon and below the lowest excited state of helium.

This could not be accounted for as a third-order process involving the two rare gases and an electron since the intensity was about 10^5 times greater than would result from such a process. We conclude therefore that the ion must arise from the reaction of an argon atom excited to a discreet state in the ionization continuum. Such states, presumably due to excitation of two electrons, have been known by spectroscopists for other elements but have not been reported for rare gases. However, recently mass spectroscopists have reported such states for argon in the energy range that we find for this reaction. For such double excitation sufficiently far above the ionization potential the lifetime of the excited state may be sufficient to permit collision and the resulting chemi-ionization reactions. NeXe^+ appears also to be formed by such a process involving a xenon atom excited to an energy level above the ionization potential. It is interesting that, with several of the ions the appearance potential occurs above the ionization potential of one of the reactants. The existence of a stable molecule above one of its possible decomposition asymptotes requires an explanation. Presumably this may result from the non-crossing rule but, of course, this is purely speculative.

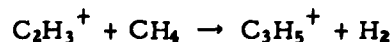
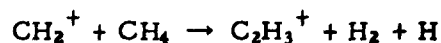
This work is complete. A technical report has been prepared and the paper submitted for publication in the Journal of Physical Chemistry.

Study of the Ion-Molecule Reactions in Light Hydrocarbons. It is planned to study the principle ion-molecule reactions in several of the light paraffins, olefins, acetylenes, etc. This program is just getting under way and a study of methane has been carried out first. Although methane has been investigated previously by Wexler⁽⁵⁾ we feel that it would be worthwhile to repeat the work, in part to establish some points of technique and, in part,

because some observations of ours disagreed with Wexler's results. We have measured the rates of the principle second- and third-order processes. It is well established that the principle secondary ions C_2H_5^+ and CH_5^+ arise from reactions



In addition we find C_2H_3^+ and C_3H_5^+ arising primarily from the reactions



We have measured the rates of these reactions quite precisely and give the results in Table 2.

As part of this study we have initiated a brief program aimed at establishing the origin of several metastable peaks in the mass spectrum of methane at higher pressure with the object of finding some metastable ions resulting from the spontaneous decomposition of the complex formed in an ion-molecule reaction. Although this work is just getting started we have found a number of metastable peaks. Most of them are due to collision induced decomposition but a few appear to result from spontaneous decomposition.

By operating at very low electron energy (just sufficient to form CH_4^+ in the primary spectrum) and about 200 microns pressure, we have been able to observe metastable peaks arising only from CH_5^+ . All are due to collision in the analyzer tube. The processes and their approximate cross sections at 2000 ev energy are

	<u>m*</u>	<u>σ (2000 eV)</u>
$\text{CH}_5^+ \rightarrow \text{CH}_4^+ + \text{H}$	15.06	6
$\text{CH}_5^+ \rightarrow \text{CH}_3^+ + \text{H}_2 ?$	13.24	2
$\text{CH}_5^+ \rightarrow \text{CH}_2^+ + \text{H}_2 + \text{H}$	11.52	.3
$\text{CH}_5^+ \rightarrow \text{CH}^+ + 2\text{H}_2 ?$	9.94	.1
$\text{CH}_5^+ \rightarrow \text{C}^+ + 5\text{H} ?$	8.47	.05

By successive small increases in electron energy metastable peaks arising from successive primary ions (or their product ions) are observed. At this time these have not been completely identified, however.

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Table 1Appearance Potentials of Rare Gas Diatomic Ions

<u>Ion</u>	<u>Ap(ev)</u>		<u>Ion</u>	<u>Ap(ev)</u>	
	<u>These Data</u>	<u>Literature</u>		<u>These Data</u>	<u>Literature</u>
He ₂ ⁺	23.3 ± 0.1	23.2 ⁽¹⁾ 23.4 ⁽²⁾	HeKr ⁺	19.9 ± 0.1	
Ne ₂ ⁺	20.9 ± 0.2	20.9 ⁽¹⁾	NeAr ⁺	16.8 ± 0.1	16.5 ⁽⁴⁾
Ar ₂ ⁺	14.7 ± 0.1	15.1 ^(1,3)	NeKr ⁺	16.6 ± 0.1	
Kr ₂ ⁺	13.0 ± 0.1	13.2 ^(1,2)	NeXe ⁺	16.0 ± 0.3	
Xe ₂ ⁺	11.2 ± 0.1	11.6 ⁽¹⁾	ArKr ⁺	14.0 ± 0.1	
HeNe ⁺	23.4 ± 0.1	22.6 ⁽²⁾	ArXe ⁺	13.5 ± 0.1	13.5 ⁽²⁾
HeAr ⁺	17.9 ± 0.3		KrXe ⁺	12.3 ± 0.1	12.2 ⁽²⁾

Table 2Rate Constants of Ion-Molecule Reactions in Methane

	<u>10¹⁰k, cc/molecule sec., based on</u>	
	<u>Reactants</u>	<u>Products</u>
CH ₄ ⁺ + CH ₄ → CH ₅ ⁺ + CH ₃	10.3, 10.1	10.6, 10.0
CH ₃ ⁺ + CH ₄ → C ₂ H ₅ ⁺ + H ₂	8.1, 8.2	7.7, 7.8
CH ₂ ⁺ + CH ₄ → C ₂ H ₃ ⁺ + H ₂ + H	10.9, 12.1	12.6, 13.2
CH ⁺ + CH ₄ → ?	15.4	
C ⁺ + CH ₄ → ?	11.0, 13.2	
CH ₂ ⁺ + 2CH ₄ → C ₃ H ₅ ⁺ + 2H ₂ + H	4.5 x 10 ⁻²⁶ cc ² /molecule ² sec.	

HIGH TEMPERATURE REACTIONS

The Pennsylvania State University, Phase I

Howard B. Palmer, Phase Leader
B. E. Knox, R. Carabetta, E. T. McHale, assistants

Introduction

The work covered in this report includes the completion of the initial objective of the single-pulse shock tube measurements of hydrazine decomposition, plus the continuation of the studies of radiative atom recombination in a conventional shock tube.

Discussion

Hydrazine decomposition. The initial objectives in the single-pulse shock tube studies of hydrazine decomposition have been completed and have provided the content for the Ph. D. thesis for B. E. Knox. Copies of the thesis have been submitted to Project Squid (1), and this work is currently being prepared for publication and will be submitted to Project Squid at a later date. The degree was conferred in March 1963.

The thermal decomposition of hydrazine was studied in a single-pulse

shock tube over a temperature range of 950° to 1160°K and a pressure range of 2.8 to 5.4 atmospheres. The decomposition products were analyzed in a mass spectrometer, and the overall stoichiometry of the homogeneous decomposition was determined to be $2\text{N}_2\text{H}_4 \rightarrow 2\text{NH}_3 + \text{N}_2 + \text{H}_2$. The detailed analytical procedure is currently being prepared for publication and will be submitted to Project SQUID at a later date. Kinetic calculations were carried out using a procedure which took into account the detailed behavior of the shocked gases; the computations were done on an IBM 7074 high-speed digital computer. This procedure has been submitted as Squid Report PSU-9-P and has also been submitted for publication in the AIAA Journal (2). Although the reaction orders were not determined precisely by experimental techniques, reasonable estimates were made by analyzing mechanisms and thermochemical data. In all probability the decomposition of hydrazine in the temperature and pressure regions studied was 3/2-order with respect to hydrazine concentration and zero-order with respect to total gas concentration. In this case the rate constant, $k_{3/2} \approx 9 \times 10^{12} \exp(-37,400/RT) \text{ cc}^{1/2} \text{ mole}^{-1/2} \text{ sec}^{-1}$. The steady-state assumption for the intermediate species in the chain was shown to be valid. The proposed mechanism included initiation by a quasi-unimolecular N-N bond-breaking process, propagation via NH_2^\cdot , $\text{N}_2\text{H}_3^\cdot$, and H^\cdot , and termination by NH_2^\cdot recombination. In conjunction with this work a study was made of the approach to the steady-state in competitive-consecutive reactions; this was submitted to the Journal of Physical Chemistry for publication and also as Squid Report PSU-10-P (3). The study of the thermal decomposition of hydrazine is being continued by Mr. McHale and is being supported by the Army Research Office-Durham.

Radiative atom recombination. Radiative atom recombination in a conventional shock tube is being studied by Mr. Carabetta. This work is directed toward determining the absolute rate and temperature coefficients for the two-body atom recombination of Cl and Br atoms. At the termination of the support by Project Squid the preliminary studies have been completed. Useful data are now obtainable. This work is currently being supported by the Army Research Office-Durham.

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CHEMICAL KINETICS AND GAS DYNAMICS OF
ATOM AND FREE-RADICAL REACTIONS

Stanford Research Institute - Phase I

Henry Wise - Phase Leader
Clarence M. Ablow
Carole R. Gatz
Dan J. Schott
Bernard J. Wood

Introduction

In the gas dynamics of propulsion systems homogeneous and heterogeneous kinetics, as well as transport properties of reactive gas mixtures containing neutral and charged particles, play an important role. Our studies of properties of gas mixtures undergoing surface and gas-phase reactions include: (1) physical and chemical interaction of atoms with solid surfaces, (2) homogeneous atom-recombination kinetics and chemionization, and (3) transport properties of chemically reactive gas mixtures. Experimentally the atoms are produced in an electrodeless discharge of the molecular gas (such as H_2 , O_2 , or N_2). The progress of reaction, i.e., the kinetics of molecule formation, is monitored by microcalorimetric (1) and electron-paramagnetic resonance (2) techniques.

Discussion

Physical and chemical interaction of atoms with solid surfaces. The application of the diffusion tube technique to the study of gas dynamics in the transition from the viscous-flow to the molecular-flow regime has been discussed in a previous publication (3). An extension of this work to the higher pressure region has demonstrated the transition from the reaction-limited to the diffusion-limited process in a system employing catalytic probes for atom detection. For the one-dimensional case the mass flux to a catalytic surface is given by

$$\delta = n_0 / [(1/k) + (L/D)] \quad (1)$$

where n_0 represents the atom density at the source, k , the surface recombination rate constant (related to the recombination coefficient $\gamma = 4k/c$, where c is the mean atomic velocity), L , the probe distance from the atom source, and D , the binary diffusion coefficient. Under certain conditions the second term in the denominator of the above equation may predominate ($L/D \gg 1/k$) and a diffusion-limited process results, i.e., $\delta \simeq Dn_0/L$. Such a process will be favored at higher gas pressure since $D \propto 1/P$ while k is independent of pressure. In our work with atomic hydrogen at 300°K such a condition is approached at a gas pressure of about 1 torr for a platinum surface, and about 0.7 torr for nickel. In this pressure region the surface recombination coefficient γ loses its defined meaning, since heterogeneous reaction kinetics no longer plays a dominant role. As expected from theoretical consideration, the mass flux becomes proportional to the diffusion coefficient, i.e., inversely

proportional to the gas pressure. Under these conditions the degree of the surface-catalytic activity merely governs the onset of the diffusion-controlled pressure region. As a result, the response of the catalytic filament as measured by the heat flux F to it can be related directly to the absolute atom density n , provided the energy accommodation coefficient is known, i.e., $F = \beta \delta$.

At low pressures, on the other hand, the mass flux as given by equation (1) approaches $\bar{x} \simeq k n_0 = \gamma c n_0/4$, so that the probe response is governed entirely by its catalytic efficiency for atom recombination. Such considerations are of importance in the application of catalytic probes for quantitative atom-density measurements in high-speed gas streams.

For the exchange of kinetic energy between a gas and a solid surface, two models have been employed in a theoretical examination of inelastic collisions. The first, based on the dynamics of a one-dimensional lattice in terms of classical mechanics, is similar to that employed by Cabrera (4) and Zwanzig (5). However, our model includes a range of mass ratios (mass of gas to mass of lattice atom), various lattice force constants, and attractive potentials, similar to the model developed by Mc Caroll and Ehrlich (6). The second analysis treats the energy transfer process in terms of a surface residence time of the incoming gas atom. It considers the impinging gas molecule to remain sorbed on the surface before it re-evaporates. Accordingly, collisional energy accommodation between solid and gas is governed by the time lag between condensation and evaporation of the gas which in turn depends on the intensity of the force field near the surface (7). Such an analysis shows interesting

correlations with recent measurements of accommodation coefficient on solid surfaces covered with an adsorbate.

Homogeneous atom-recombination kinetics and chemionization. An important experimental approach to the understanding of multi-body collision processes is to be found in the study of the kinetics of homogeneous atom recombination. A series of experiments has been completed on the hydrogen atom system in an attempt to elucidate the third-body efficiency of atomic and molecular hydrogen. Catalytic probe measurements have been employed to obtain the atom-concentration profile in the cylindrical reaction chamber through which the gas mixture (H and He) is flowing. It has been observed that in the pressure range of interest ($3 < P < 10$ torr) the atom flux to the probe is diffusion controlled (cf. preceding section). At 300°K the results yield a rate constant for the gas phase reaction $k_g = 8 \times 10^{15} (\text{atom/cc})^{-2} \cdot \text{sec}^{-1}$, and for the surface reaction $k_s = 1.5 \times 10^2 \text{ cm} \cdot \text{sec}^{-1}$. The latter value compares favorably with the result obtained in other independent measurements of hydrogen-atom recombination on Pyrex glass (8). Also an appreciable loss in atom concentration due to wall reaction was noted. As a result the theoretical analysis previously developed (9) needs to be extended to include radial diffusion with heterogeneous atom recombination in addition to gas-phase recombination.

Studies of the kinetics of chemionization resulting from the reaction of nitrogen atoms with nitric oxide have shown the contribution of three-body, single-step reactions and two-step mechanisms. The results of these measurements have been incorporated in a publication (10); the conclusions are in qualitative agreement with recent measurements obtained by a different experimental technique (11).

Transport properties of chemically reactive gas mixtures. The "hot filament technique" is being applied to the determination of the thermal conductivity of gas mixtures containing atomic and molecular hydrogen. By suitable choice of filament material and cylinder walls (in terms of catalytic properties) the mass-flux vector of atoms may be adjusted to coincide with or to oppose the energy-flux vector. For metal filaments a thin deposit of silicon monoxide effectively poisoned the surface for hydrogen-atom recombination. In such a way the variation in heat transfer coefficient may be explored. In the presence of a non-catalytic hot filament and for mole fraction of atomic hydrogen less than 20 per cent, little variation in thermal conductivity of the gas mixture was noted. This observation is of considerable importance to the application of catalytic calorimeter techniques to atom-concentration measurements (cf. section 1).

The heat conductivity measurements have been extended to a three-component system containing H, H₂, and Ar. For gas mixtures of different composition containing H₂ and Ar (in the absence of H) the relative thermal conductivities were found to be in good agreement with published data. For the three-component system the experimentally determined conductivities followed a theoretical curve constructed on the basis of collision cross sections and mixture rules for transport parameters (12, 13).

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INELASTIC MOLECULAR COLLISIONS

The University of Virginia - Task Order 1

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John A. Phipps

Introduction

The general objective of this program is the examination of inelastic molecular collisions using molecular beam techniques. The gas phase interaction of colliding molecular or atomic species is to be examined for those collisions in which sufficient energy is supplied such that a rearrangement of atomic bonds takes place (1). An aerodynamic molecular beam source is to be used in order to provide a nearly isoenergetic beam of neutral particles of large intensity. A mass spectrometer is to be used to detect the products of an inelastic collision. Reaction cross sections are to be determined as a function of the energy available in the collision system

Discussion

The differential ionization gauge detector, using two commercially available Bayard-Alpert gauges, has been demonstrated to be a reliable

device for the measurement of intensities of molecular beams formed with atmospheric gases. These results were presented at the Third International Symposium on Rarefied Gas Dynamics (2). The detector sensitivity, when adjusted linearly for minor changes in gauge emission current, has been shown to be consistent and reproducible to less than 1% over long periods of time even with significant changes in beam geometry. Furthermore, the sensitivity values agree with those quoted by the gauge manufacturer within about 5%, a condition considered to be good agreement. The spurious effects observed in the formation of effusion beams used for detector calibration purposes which were reported previously (3) have been resolved by careful measurement. The useable sensitivity of the detector is very high; e.g., for an effusion beam of nitrogen at a source pressure of 10^{-2} mm Hg, the detector pressure difference is about 2×10^{-10} mm Hg. Hence, the detector is capable of measuring pressure differences of the order of 10^{-10} mm Hg when the background pressure is 10^{-7} mm Hg. Furthermore, this sensitivity has been improved even more by long-term continuous pumping on the detector vacuum chamber. At present, it is possible to detect beams whose flux is as low as 10^{10} molecules/sec. Such a sensitivity is very important for reliable beam scattering experiments or for the measurement of the complete velocity distribution in aerodynamic molecular beams.

On the basis of results obtained with a beam source of modest pumping capacity, a new and improved apparatus has been completed in order to realize more closely the potential advantages of the aerodynamic beam source. Emphasis was placed on the improvement of pumping capacity of the collimator and nozzle discharge chambers. The total flux of beams of

nitrogen has been measured for various nozzle source pressures as a function of the distance between the nozzle exit plane and the entrance to the skimmer or first beam aperture. It has been shown theoretically by Owen and Thornhill (4) that the thermodynamic and aerodynamic characteristics of the nozzle flow can be expressed in terms of the distance downstream of the nozzle. Furthermore, Fenn and Deckers (5) have verified these results experimentally except for conditions where the nozzle source pressure is very low and/or the nozzle-skimmer displacement distance is very large. Consequently, the nozzle-skimmer displacement distance can be used to estimate the skimmer Mach number which, in turn, can be used to enable the comparison of the measured beam flux to that computed theoretically. The beam flux data for a fixed nozzle source pressure exhibit three more-or-less discrete parts. At short distances, the beam flux decreases with increasing distance until a minimum occurs. At larger distances, the beam flux increases again to some maximum value. Further increases in nozzle-skimmer separation distance result in a decrease in beam flux. These three regions of beam operation correspond roughly to flow regimes at the skimmer entrance which are continuum, slip-transition, and free molecular, respectively. Beam intensities of 10^{17} molecules/sec/cm² have been observed. Correlation of the data based on the Mach number determination of Owen and Thornhill (4) indicates that the beam flux increases linearly with M^2/Kn for all values of the nozzle source pressure provided that $Kn \gg 1$ or that $Kn \ll 1$. In the intermediate range where $(1 > Kn > 0.2)$ no correlation is obtained. The ratio of the measured flux to the computed value varies between 0.05 and 0.50 depending on the source pressure and nozzle displacement. In general, the experimental

results tend to approach the theoretical predictions at large values of the skimmer Knudsen number. Angular distributions of beam intensity indicate that as the nozzle-skimmer distance is increased, the beam width is decreased; and the peak intensity increases. However, at large distances, the peak intensity decreases again although the beam half-width does not change appreciably from its best value. These results suggest that the skimmer Mach number does not increase continuously with increasing nozzle-skimmer displacement as indicated by the calculations of Owen and Thornhill (4). Rather, dissipation of the nozzle flow may occur which results in a decreased effective skimmer Mach number at large distances, a phenomenon observed and suggested by Bier and Hagena (6). Description of the nature of the flow field at the skimmer entrance will require further study. Beam velocity distribution experiments should be particularly useful in this respect.

The mechanical velocity selector, designed and constructed in cooperation with a program sponsored by the Bureau of Naval Weapons, Code RRRE, has been completed; and a large quantity of velocity distribution data has been obtained on aerodynamic molecular beams during the current contract period. The selector is capable of measuring speeds up to 4.5×10^5 cm/sec with a resolution of 10% and a minimum transmission of 55%. Furthermore, the selector geometry is such that all submultiples of the desired speed are not transmitted. Initial experiments were performed with nitrogen beams at various nozzle source pressures at a fixed nozzle-skimmer separation distance of about 16 nozzle diameters. The distribution of molecular velocities in these aerodynamic beams exhibit the salient features predicted theoretically; i. e., the velocity distributions in aerodynamic beams are more narrow than

the corresponding effusion beam, and the most probable speed is increased significantly. Hence, the production of ordered motion in the formation of aerodynamic molecular beams has been demonstrated not only by increased beam intensities, but by an improved velocity distribution as well. However, the effective skimmer Mach number indicated by the measured velocity distributions is much lower than that expected on the basis of the Owen and Thornhill theory (4). Furthermore, the distribution widths are more narrow than would be expected on the basis of the observed most probable speed. These results suggest, first, that a dissipative process may be occurring in the nozzle flow which decreases the effective ordered motion at the skimmer entrance, the same effect noted above on the basis of total beam intensity measurements. Secondly, the unusually narrow nature of the measured distribution suggests the possibility of significant rotational relaxation during the rapid nozzle expansion process. This phenomenon would result in the gas having an effectively larger ratio of specific heats which would, in turn, result in a more narrow distribution. As a check on this point, the distribution of molecular velocities in a large number of aerodynamic beams of argon have been determined. It has been found that the measured distributions can be represented by the theoretical distribution function with the proper specific heat ratio ($5/3$ in this case) and observed source temperature. Consequently, it has been shown that even though the total beam flux does not agree with the value computed theoretically, the distribution functions do check when proper account is taken of the amount of ordered motion in the beam. The effect of nozzle-skimmer displacement on argon beams has been measured, but the data reduction process is not yet complete. Similar experiments with nitrogen

and, perhaps, hydrogen are planned. Even at this early stage, however, it is important to note that the velocity distributions in aerodynamic beams do in fact have the essential characteristics predicted theoretically. This is an important result in terms of the scattering experiments planned with these beams.

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SOLID-PROPELLANT FLAME MECHANISMS

Atlantic Research Corporation - Phase 4

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Introduction

The objective of this program is to gain basic information pertinent to solid-propellant combustion mechanisms by studying combustion of single metal particles (aluminum or beryllium) injected into flame gases of known temperature and composition.

Discussion

Determination of the ignition limit of spherical aluminum particles (diameter range of 30 to 45 micron) at elevated pressures by a previously developed method (1) has been completed. The method consists of admixing small amounts (0.05 to 0.2 per cent) of aluminum to a combustible oxidizer-fuel mixture which is then burned in loosely tamped powder form. The ambient conditions necessary for ignition of the metal have been determined at 1, 5, 10, 50, and 100 atmospheres pressure. It was found that, as the partial pressure

of oxygen increased from a small fraction of an atmosphere to 16 atmospheres, the minimum ignition temperature decreased from 2300 to about 2050° K. For total pressures in excess of about 50 atm, the minimum ignition temperature is quite insensitive to variation in either the total pressure or the partial pressure of oxygen. These results can be readily interpreted in the light of a previously published theory of ignition (2).

The same method, utilizing low-density powder mixtures, has been adapted to combustion of beryllium particles of approximately the same diameter range as aluminum. In view of the higher ignition temperature of beryllium, powders containing a higher ratio of fuel to oxidizer have been used to provide hot ambient gases. The range of ambient conditions needed for combustion of beryllium, accessible by the above outlined method, is as follows: temperature from 2300 to 2800° K, total pressure from 2 to 100 atmospheres, and partial pressure of oxygen from a small fraction of an atmosphere to about 6 atmospheres.

Safe handling of beryllium and its combustion products presents a major problem. An apparatus conforming to stringent industrial hygiene requirements has been constructed which allows the beryllium-containing powder to be ignited in a sealed capsule. Dilution required for disposal of combustion products is 1 part of beryllium in a million parts of water or 25 micrograms of beryllium in one cubic meter of air. The combustion products contained in the air-tight burner are therefore flushed first with a stream of nitrogen through a dry filter, and then with generous amounts of water, all without opening the burner. Analytical safety monitoring of the equipment after these cleansing procedures has shown the contamination level to be well within the acceptable limits, and burning of beryllium has begun.

Results of ignition of beryllium particles show the process to be significantly affected by the concentration of oxygen in the ambient gas. The metal ignites at temperatures as low as 2380°K when the partial pressure of oxygen is about 6 atm, and only above 2650°K when partial pressure of oxygen is less than about 0.1 atm. Thus in fuel-rich mixtures the temperature limit for ignition approaches the melting point of BeO (2820°K) and also the normal boiling point of beryllium (2760°K).

The mode of combustion is also affected by the ambient conditions. Large excess of oxygen appears to accelerate the burning. At low concentrations of oxygen and high temperatures, metal particle tracks are sharp and straight on photographic exposures, a characteristic of surface combustion of metals. At high oxygen concentrations and relatively low temperatures the light from the burning particle is often intermittent and fairly diffuse.

So far, all ambient temperatures reported in this program were the computed adiabatic flame temperatures of the fuel mixtures, gaseous or solid. For experimental verification, an optical line-reversal apparatus has been assembled and is being tested. The apparatus will allow temperature measurement to about 2600°K. An independent temperature check for the pre-mixed propane flame has been made by determination of the melting point of platinum. Fine platinum wires were found to melt at calculated temperatures (including radiant heat loss from the wire) of $2090 \pm 10^\circ\text{K}$ and $2020 \pm 10^\circ\text{K}$ in fuel-lean and fuel-rich flames, respectively. The accepted melting point of platinum is 2040°K.

Future plans include a more detailed study of the ignition and combustion of beryllium particles. An attempt will be made at a study of

the burning rate of aluminum, and possibly also beryllium, particles by sudden quenching of such particles at different stages of combustion, and subsequent chemical micro-analysis of partly burned samples.

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THERMAL CONDUCTIVITIES OF GASES
AT HIGH TEMPERATURESUniversity of Delaware - Phase I
Task Order No. Nonr-3623(S-14)J. R. Ferron, Phase Leader
Bernhard J. Kraus
Jay R. BalderIntroduction

Thermal conductivities of carbon dioxide and of mixtures containing CO_2 are being studied at one atmosphere and 1000-1800 °K with an apparatus like that used previously for diffusion research (1,2). Temperature of a laminar stream of hot gas is caused to vary from point to point, and measurements of temperature profiles yield data from which thermal conductivities may be computed.

A second experiment similar to that of several previous workers (3) utilizes a shocktube for thermal conductivity studies. One observes the surface temperature of a block of pyrex during the brief interval of time in which the pyrex and an incident shock wave of gas might be considered to be like two semi-infinite, isothermal media brought suddenly together. The temperature-time behavior of the pyrex-gas interface provides data from which thermal conductivity of the gas can be determined.

Discussion

The preliminary experiments with the first apparatus, described in the previous Semi-Annual Report, have been completed; and we are making equipment changes preparatory to beginning actual measurement of thermal conductivities.

Temperature uniformity in the measuring section is not as good as we would like to obtain, but it is probably sufficient to allow the first exploratory set of measurements to be made. Similarly our errors in temperature measurement are larger than we would like eventually to realize but not so large as to cause delay of the first set of measurements. It is important that we proceed to these relatively crude initial measurements because they may disclose need for additional equipment changes unrelated to temperature uniformity or to accurate temperature measurement.

Electronic difficulties with the shocktube apparatus appear to have been overcome; we are currently getting what look to be excellent data. The usual driver gas is helium, but nitrogen gives a measurable shock of comparatively low temperature. Use of either or both gases should yield a continuous range of gas temperatures of 800-2000 °K. This range effectively overlaps that of prior low-temperature measurements and that of the high-temperature measurements with the combustion apparatus. The shocktube measurement should serve well, then, as an independent check on the validity of results from the combustion apparatus.

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MAGNETOHYDRODYNAMICS OF PARTIALLY IONIZED GASES

Massachusetts Institute of Technology - Phase 3

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J. B. Workman

Introduction

At present the efforts of this group are devoted to basic theoretical and experimental studies of the important physical phenomena arising in magnetohydrodynamic propulsion and power generation machines.

The theoretical investigations are centered on a study of the unsteady wave motion in the presence of electric and magnetic fields. The experimental portion of the work is focused on the utilization of combustion driven shock tubes to duplicate in the laboratory those conditions of gas velocity, temperature, density and electrical conductivity which might prevail in an actual device.

Discussion

Earlier studies of ionization in seeded detonation waves showed that the shock tube was a simple, easily operated research tool, the primary limitation being the shortness of the available test time. To partially overcome this limitation, a "piggyback" tube has been constructed in which test times an order of magnitude greater than those obtainable in a conventional tube have been attained. The useful operating range and some of the observed gas and flow properties are presented in the following table (data is for argon).

Unshocked Gas Press. (mm. Hg.)	Shock Mach No.	Particle Velocity (ft/sec)	Electrical Conductivity (mho/m)	Test Time (μ /sec)	Slug Length (ft)	Gas Temp. (°K)
8	9.5	7,430	7.6	1840	15	8,800
1	11.5	10,100	15	350	3.6	10^4
0.1	14	12,900	33	40	0.5	10^4

A magnetohydrodynamic ($\vec{j} \times \vec{B}$) accelerator section approximately 2 feet in length has been constructed, and is being used in conjunction with the shock tube to assess the degree and efficiency of acceleration, the change in gas and flow properties, and the nature of the discharge phenomena in the working section. Measurements of upstream and downstream velocity and luminosity are being made by means of ionization gages and photomultipliers respectively, and field-search coil combinations are being used to determine the gas electrical conductivity. In addition, rotating mirror camera photographs of the

flow in the working section are being taken in a plane perpendicular to that of the electrodes. Magnetic field strength and electrical power input to the accelerator are evaluated by measuring currents and voltages in the respective circuits.

As indicated in the previous report, an analysis of unsteady motion of shock-heated gases has been commenced, and solutions for the linearized equations corresponding to small perturbations have been obtained. The scope of this investigation has been broadened to include the case of waves which steepen to finite amplitude in the presence of magnetic fields with directions other than tangential to the wave front. In particular, the case of switch-on shocks is being examined in some detail. In such a shock, the tangential components of velocity and magnetic field jump from zero in front of the shock to some finite value behind.

A paper describing the principles and current state of the art of magnetohydrodynamic power generation has been accepted for presentation at the annual meeting of the Engineering Institute of Canada.

ENTHALPY FLUCTUATIONS IN PLASMA JETS

University of Minnesota - Phase I

Perry L. Blackshear, Jr., Phase Leader
William H. Kuretsky, Gordon O. Voss
Dah Yu Cheng, Frank D. Dorman

Introduction

This research program is concerned with the use of immersion instruments to measure enthalpy fluctuations in time and space in high temperature gases. The basic sensing element developed during the course of this research is an internally cooled thin film anemometer capable of withstanding heat transfer rates on the order of those found in liquid propellant rocket chambers. This sensing element has been installed in a probe with transpiration cooled walls in such a way that the sample gas is diluted with a coolant and passed by the sensor in a small mixing chamber. This assembly has been called a mixing probe, and is capable of withstanding an indefinitely high temperature environment.

The time response of the mixing probe depends on the filling and emptying time of the mixing chamber. The present designs have filling times on the order of $1/5,000$ of a second. The heat flux probe in such an installation is capable of detecting fluctuations of enthalpy about a mean. Owing to the inaccuracies inherent in interpreting heat transfer data it is not particularly well suited for establishing the magnitude of the mean enthalpy. The investigation described in the present phase represents an attempt to more accurately determine the mean enthalpy of the hot plasma approaching the mixing probe.

Discussion

Mixing Probe. The basic mixing probe with a single thermocouple sensor has been described in Reference I. In this probe it is assumed that the temperature measured by a single thermocouple placed near the exit of the mixing chamber gives a representative temperature of the gas within the mixing chamber. This temperature along with the analysis of the entire gas which leaves the mixing chamber permits a determination of the average enthalpy of the gas entering the mixing chamber.

A traverse of the mixing chamber with a tiny thermocouple has shown that a temperature profile existed such that the temperature in the mixing chamber was lower near the mixing chamber walls and higher in the center. In an effort to obtain a more representative relationship between temperature and composition, the thermocouple was mounted in a small sampling tube such that thermocouple and gas analyzer both viewed the gas drawn locally from within the mixing chamber. This data again permitted the calculation of the enthalpy of the gas entering the mixing probe for each position of the small sampling tube within the mixing probe. Experiments showed that despite the fact that temperature and composition varied across the mixing section, a calculation of up-stream enthalpies were substantially constant, no matter where the sampling probe was positioned. This design alleviates the problem of precisely positioning the thermocouple sensor.

Test Section. A 12 KW commercially available plasma jet with a 1/4 inch orifice, a water cooled anode employing argon gas, was used as the high temperature gas source to permit a determination of the time constant of the thermocouple probe system. A shunting resistor was placed in the power supply of the plasma jet such that a step in power can be imposed. A further

modification consisted of enshrouding the plasma jet orifice with an annular helium jet such that in the region immediately above the plasma jet orifice a mixture of argon and helium should exist to the exclusion of surrounding air. Subsequent data showed that the helium jet did not accomplish this function and is presently being redesigned.

Gas Analyzer. A thermal conductivity gas analyzer has been constructed utilizing four thermal elements, two in a helium leg and two in an argon leg. In both the helium and argon legs the unknown mixture is introduced in the stream between the two elements. With this arrangement it is possible to minimize the effect of fluctuations in pressure in the thermal conductivity cell and introduces the possibility of analyzing a tertiary mixture.

The cell has been used in such a way that it detected the presence of something other than argon or helium in the region over the plasma jet where measurements were made, and also gave the relative amounts of argon and helium in the sampled gas.

Measurements in Plasma Jet. One complete set of measurements has been made to evaluate the several components of our system. The jet was run such that neglecting radiation and ionization, the temperature could be made to switch from 23,000 to 19,000° R. The measurements made along the axis of the plasma jet indicated there was indeed a step change in temperature equivalent to a 4,000° change. In this run helium was used both as the diluent in the mixing probe as well as the shielding gas in the annular jet surrounding the argon jet. Had the mixing in the jet been altogether turbulent, we would have expected a Lewis number of unity there and the mixing probe should have indicated a constant temperature along the entire axis of the jet.

The data, however, showed a sharp decrease in temperature above the jet, the maximum temperature being $20,000^{\circ}\text{R}$, falling off to $4,000^{\circ}\text{R}$ 3 inches away from the jet. The reasons for this discrepancy between anticipated and obtained results is being explored.

Notes and References

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TECHNICAL REPORTS

October 1, 1962 - March 31, 1963

Semi-Annual Progress Report

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<u>Number</u>	<u>Title and Author</u>	<u>Microcard Dist. Date</u>	<u>Other Presentation () Indicates Plans</u>
ARAP-4-P	A New Approach to Non-Equilibrium Statistical Mechanics of Gases - J. E. McCune, G. Sandri, and E. A. Frieman	11/62	Third Int'l. Symp. on Rarefied Gas Dynamics (1962)
ARAP-5-P	Energy and Momentum Exchange Between Non-Equipartition Gases - F. T. Morse	3/63	(Phys. of Fluids)
BRN-1-P	The Viscosity of Superheated Steam up to 275°C. A Refined Determination - J. Kestin and P. D. Richardson	11/62	(ASME J. of Heat Transfer)
BRN-2-P	A Relative Determination of the Viscosity of Several Gases by the Oscillating Disk Method - J. Kestin and J. H. Whitelaw	11/62	(Physica)
BRN-3-P	The Viscosity of Nitrogen, Helium, Neon, and Argon from -78.5°C to 100°C below 200 Atmospheres - G. P. Flynn, R. V. Hanks, N. A. Lemaire, and J. Ross	1/63	J. of Chemical Physics, vol. 38, no. 1, p. 15, (1963)
CAL-86-P	Combustion of Metals - G. H. Markstein	1/63	ARS Meeting (1962)
HUM-1-P	A Mass Spectrometric Study of Homonuclear and Heteronuclear Rare Gas Molecule Ions - M. S. B. Munson, J. L. Franklin, and F. H. Field	3/63	(J. of Physical Chemistry)
ILL-9-P	A Study of Concentration and Mass Flow Distributions in a Gas - Solid Suspension - S. L. Soo, G. J. Trezek, R. C. Dimick, and G. F. Honnstreiter	3/63	(Am. Chemical Society, 1963)
MIT-29-P	Magnetohydrodynamic Power Generation - Its Principles and Problems - W. C. Moffatt	1/63	(The Engineering Journal) (Engineering Inst. of Canada, 1963)

<u>Number</u>	<u>Title and Author</u>	<u>Microcard Dist. Date</u>	<u>Other Presentation () Indicates Plans (ARS Journal)</u>
PSU-9-P	Computation of Kinetic Constants from Single-Pulse Shock Tube Data - H. B. Palmer, B. E. Knox, and E. T. McHale	2/63	
PSU-10-P	Approach to the Steady State in Competitive-Consecutive Gas Reactions - H. B. Palmer	3/63	(J. of Physical Chemistry)
SRI-14-P	Energy Accommodation in Exothermic Heterogeneous Catalytic Reactions - B. J. Wood, J. S. Mills, and H. Wise	1/63	(J. of Physical Chemistry)
SRI-15-P	Energy Exchange Between Gases and Solids - H. Wise	3/63	(J. of Physics and Chemistry of Solids)